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CELL PERFORMANCE OF ULTRA-THIN POLYMER CATHODE SYSTEMS PART I. ANION INTERCALATING POLYMER CATHODE

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ABSTRACT

Theoretical energy and power density values for thin film Li/liquid electrolyte, polymer cell systems were calculated by designing a specific cell model for a both prismatic cell with only the basic cell element(no hardware) and a bipolar-design cell with some practical hardware. The cell performance is compared for three different cathode polymer materials, viz., polyaniline, polypyrrole, and polyvinylferrocene. The energy and power densities are estimated as a function of cathode thickness, active cell area, and initial concentration of electrary terror yet for very thin cathode films (cathode thickness: L_c=1 to 100µm). For the practical cell, the authors used a bipolar design, for which the energy and the power were calculated also as a function of the number of bipolar units(X). Optimization of the cell performance was attempted, and optimal values for Lc, S, and X are proposed. For the Li/4M LiClO₄(PC)/Polyaniline(without hardware), energy densities were 152 Wh/kg and 290 Wh/liter. Specific pulse power for the same cell amounts to 160 MW/kg. As for bipolar-design Li/4M LiClO₄(PC)/Polyaniline cell(with hardware), the optimum values for projected specific energy and power was found to be ca. 120 Wh/kg and 1.5 MW/kg, respectively for 10 bipolar unit with 10 µm cathode thickness and 100 cm² electrode area.

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INTRODUCTION

Conducting polymers as well as redox polymer materials are regarded to have high electroactivity in organic liquid electrolytes 1-17. These materials can be utilized as one of the promising candidates for cathode materials in future rechargeable cell systems. Polymer cathode cells, in general, are known to have a lower energy density when compared to inorganic intercalation materials such as the oxides or sulfides of Ti, Mo and V. However, this type of conducting polymer material has very fast kinetics in exchanging electrons as well as ions during the charge/discharge process, especially when the polymer film becomes very thin(of the order of microns). The rapid kinetics should lead to high power densities. So, this type of polymer material is considered to be a high power material rather than a high energy material. This paper involves theoretical calculations of energy and the specific power for secondary lithium cells using three different polymer cathode materials. The polymer materials were selected on the basis of our previous results. Three different categories of polymers, viz., polypyrrole¹⁻¹³:PPy (heterocyclic conducting polymer), polyaniline ¹⁴⁻¹⁶: PAn(ionen polymer) and polyvinylferrocene ¹⁷: PVF (redox polymer) are used. These three polymers represent different features in their structure, electrochemical response, and physical properties. Particular emphasis of this paper is to clarify how much energy or power one may obtain from these polymer materials and the optimum conditions for certain of the fundamental cell design parameters including thickness and area.

1. Cell Model for Li/Liquid Electrolyte/Polymer Cells

One has many choices of cell construction, but in this report, we specified the following configuration, viz., Li/LiClO₄(PC)/Polymer cell. The anode material is lithium and the electrolyte is LiClO₄ in a propylene carbonate solution. The cathode material is one of the conducting polymers of high electroactivity and relatively low equivalent weight, as compared to other conducting polymer materials. Here, polypyrrole, polyaniline and polyvinylferrocene were selected as cathode materials. The cell reaction is illustrated in Fig.1 for the Li/LiClO₄(PC)/Polypyrrole cell. The charging reaction involves the oxidation of the cathode polymer with the concurrent insertion of anions from the electrolyte solution, and in the reduction process, the electroactive cathode material gives up the doped anion at the same time. So, the charge process for this cell system is essentially an electrolyte-consuming process, and the maximum level of anion uptake or oxidation/reduction state of the polymer cathode is defined by the doping level(y).

Since this polymer cathode cell is an electrolyte-reacting system, the total equivalent cell weight includes a large percentage of electrolyte salt and solvent. The equivalent cell weight (W_{eq} [g/Faraday]) is characterized by the following equation for Li/B M LiClO₄(PC)/Polymer cell;

$$W_{eq} = W_c + W_e + W_a$$

$$= \frac{100M_c}{y_{max}} + (105.95 + \frac{1198}{B}) + 6.95$$

$$= \frac{100M_c}{y_{max}} + \frac{1198}{B} + 112.9$$
(3)

where W_c , W_e and W_a are the equivalent weight contributions of the cathode, electrolyte and anode, respectively, M_c is the unit molecular weight of polymer and B is the initial concentration of electrolyte in the fully discharged cell in M(mole/dm³). The equivalent cell weight is plotted against the initial electrolyte concentration for the polypyrrole cell (M_c =65; y_{max} =33%) as shown in Fig.2. Of course, from Eq.3, a low weight cathode polymer (small M_c) and high doping level material(large y_{max}) will reduce the value of W_{eq} . Also as the electrolyte becomes more and more concentrated, the total equivalent weight of the cell decreases. For example, for a 1M LiClO₄(PC) solution, the electrolyte occupies ca. 80% of the total weight, whereas with initial concentrations of 2 and 4M respectively only 66 and 50% of the total weight is electrolyte. Therefore, by using a concentrated electrolyte solution, one should obtain higher values for energy and power density. However, there are two main limitations to use of a concentrated solution. First, concentrated solutions have high viscosity and this leads to low conductivity. Second, concentrated LiClO₄ in PC is not chemically stable, and may exhibit safety problems. Considering the above, the electrolyte concentration would be best in the region of 2 to 4 M.

For an anion-consuming reaction, the concentration as well as the conductivity changes during the charging(doping) and discharging(undoping) processes. Since we take into account the weight of electrolyte as a minimum weight required to dope the polymer, the concentration of electrolyte changes from the initial state(1,2,3, or 4 M) to 0 M when the cell changes from the fully discharged state to the fully charged state. In a practical cell, there would be provision for excess electrolyte to permit operation over the entire doping range.

The theoretical projections for both specific energy and power are made for two types of cell configurations. One is a unit cell without hardware(see Fig.3), and the other is a bipolar-design cell with some hardware(see Fig.4). The theoretical energy and power density calculations are relatively straightforward for a prismatic cell without hardware or separator. Prismatic cells only involve the cathode, electrolyte and anode as shown in Fig.3. In this case, S is the electrode area, L_c is the cathode thickness, and B is the electrolyte concentration(fixed at 4M). Figure 4 shows the battery construction of the bipolar-electrode cells which were used for the energy and power calculations of the Li/PAn cell system. Two kinds of hardware are included in this type of cell, namely, the current collectors and the case wall. The current collector(CC) involves the plates of Ni and the Al bipolar intercell connector. The Ni current collector is much harder and more dense than the Al current collector, and is better suited for a terminal electrode. On the other hand, the Al current collector is more flexible and lighter, and the thickness was assumed to be 20% of the active cell thickness(L_{cell}), unless the $L_{cell} > 150 \,\mu m$, otherwise the thickness of Al was fixed at 30 µm. For the wall material, the author used a synthetic resin(d=0.8 g/cm³), which encapsulates the entire cylindrical battery. For electrolyte solution, 4 M LiClO₄(PC) is used in the fully discharged state of the cathode. The anode material is lithium and polyaniline is the cathode material.

2. Unit Cell with Basic Cell Elements(without hardware)

The theoretical specific energy(ED) [Wh/kg] for the Li/B M LiClO₄(PC)/Polymer cell can be generally expressed as follows assuming the cell reaction described in Fig.1;

ED =
$$\frac{26.8 \text{ E}_{ave}}{W_{cell} \times 10^{-3}}$$
 = $\frac{26.8 \text{ E}_{ave}}{(112.9 + \frac{100M_c}{y_{max}} + \frac{1198}{B}) \times 10^{-3}}$ (4)

where E_{ave} is the average value for the theoretical voltage during discharge. The total cell weight (W_{cell}) can be calculated as $W_{cell}=112.9+\frac{6500}{y}+\frac{1198}{B}$ [g] for polypyrrole(Mc=65).

The doping level(y) is related to the coefficient, n, in the cell reaction of Fig.1 by $y = \frac{100}{n}$.

Fig. 5 shows the variation in ED value for three different cathode systems as a function of the initial concernation of electrolyte. As shown in all figures, an increase in the doping level is most effective in the range of 0 to 40%, with relatively little gain after 50%. However, an increase in initial salt concentration(B) can make the ED values much more efficient, compared to the effect of doping level. This is because most of the weight of the cell is occupied by the electrolyte as previously explained in Fig. 2.

Specific Energy of Cell Systems

Figure 6(left) shows the ED values for three polymer cathode cells where the initial concentration of electrolyte is 4 M. The graphs are plotted against doping level taking into account the maximum doping level for each polymer material. In terms of doping level, PVF shows the highest value(100%). However, PVF has the largest monomer weight($M_c=212$), so the ED value of the cell with PVF(ca.120 Wh/kg) is less than that of PAn(ca. 152 Wh/kg). The Li/PPy cell shows smaller values for maximum doping level,

average cell voltage and ED value. The energy density were also calculated on the basis of volume as shown in Fig.6(right). This graph also takes into account the limitation of the doping level. Interestingly, the relative values for Li/PVF are reduced by more than 50 %. This is because PVF has a relatively low specific gravity (0.42 g/cm³) compared to the other polymers: the densities of polypyrrole and polyaniline are 1.48 and 1.08 g/cm³, respectively.

Specific Pulse Power

Figure 7 shows a generalized load curve for voltage vs. current curve. The maximum power during a short pulse is shown, if one assumes the only significant polarization is due to the IR drop in the electrolyte during the pulse¹⁸. In this case, the maximum power density is obtained at the half value of voltage($\frac{E_{oc}}{2}$) and current($\frac{I}{2}$). The IR_{sol} is expressed as Eq.5. The maximum specific power of the system is finally expressed as Eq.8.

$$I R_{sol} = E_{oc} - \frac{1}{2} E_{oc} = \frac{1}{2} E_{oc}$$
 (5)

$$R_{sol} = \rho \frac{L_e}{S} \tag{6}$$

$$I = \frac{1}{2} E_{oc} \frac{S}{\rho L_e} \tag{7}$$

$$PD_{max} = \frac{E_{oc}}{2} \frac{I}{2} \frac{1}{W_{ceil}} = \frac{E_{oc}^2}{4} \frac{S}{\rho L_e} \frac{1}{W_{ceil}}$$
 (8)

where ρ is the resistivity of the electrolyte, L_e is the electrolyte thickness, and S is the area of electrode. If one considers a cell with a capacity of 1 Faraday(96500 coulombs, or 26.8 Ah), the W_{cell} for Li/4M LiClO₄(PC)/Polymer cell can be derived as Eqs.9, 10, and 11, assuming that the excess factor is unity, viz., Qcathode=Qanode.

$$W_{cell} = W_c + W_e + W_e \tag{9}$$

$$W_{cell} = W_c + W_e + W_a$$
 (9)
= $W_c \left[1 + \frac{y_{max}}{100M_c} (6.95 + 105.95 + \frac{1198}{B})\right]$ (10)

$$= d_c S L_c \left[1 + \frac{y_{max}}{100M_c} (112.9 + \frac{1198}{B})\right]$$
 (11)

 PD_{max} values are calculated for the same polymer cathode systems above. Fig.8 shows the plots of PD_{max} value vs. cathode thickness. The Li/PVF cell system has the highest values. For the PVF cathode, we can reach about 10 MW/kg at 20µm of cathode thickness. If we make the cell with a lum cathode, the projected specific power pulse approaches a order of GW/kg. The PD_{max} for the Li/PAn and Li/PPy systems look very similar because the densities of the polymer materials are similar. Fig.9 summarizes the values of PD_{max} for three different Li/polymer cathode cell systems, where the thickness of each cathode material is fixed at 1, 10 and 100µm. The reason why the Li/PVF system has such a high value is related to the low density cathode and resultant thinner region occupied by the electrolyte. Fig.10 shows the relationship between cathode thickness(L_c) and the electrolyte thickness(Le) for the three systems. Obviously, in the case of the PVF cathode system, the Le value is less than those of PAn and PPy cathode systems. The fact can be

attributed to the bulky nature of PVF(d=0.42 g/cm³); the PD_{max} is inversely proportional to L_e, as shown in Eq.8., and directly proportional to S, which is larger for the higher equivalent volume cathode material.

3. Bipolar-design Battery(Li/4M LiClO₄(PC)/PAn)

A more practical cell configuration would consist of the cell plus some basic hardware. In this section, the authors calculate the energy and power densities for bipolar-design cell which consists of (X+1) cells in series. There are X bipolar cells plus the terminal electrodes; this type of cell reduces to a single prismatic cell design when the number of bipolar units are equal to 0. The following assumptions were made for this battery design; Coulombic balance: $Q_{Li} = 3Q_{cathode}(f_{ex} = 3)$, Hardware: CC(Current collector) for terminal electrode=Ni(25 μ m thick; 1mm wider than R_{cell} ; CC in bipolar unit=Al(20% of L_{cell} (1mm wider than R_{cell}); Case=synthetic resin($R_{case} = R_{cell} + 2$ mm), where R_{cell} is the radius of the circular cell.

The calculation procedure for specific energy and power is illustrated in Fig.11 as 2 function of the number of bipolar units(X), the surface area of the active cell(S), and the cathode thickness(L_c). The calculation procedure takes into account the hardware, so, it is a little more complicated than the unit cell without hardware as calculated in section 2.

Specific Energy

There is a general tendency that as the number of bipolar unit increases, and as the area of cell increases, the specific energy values increases. The specific energy value for Li/LiClO4(PC)/PAn battery is shown as a function of number of bipolar units in Fig.12 for different cathode thickness $(1,10,100~\mu m)$ and different surface areas (1,10,100,1000,1000,1000) cm². In terms of cell areas, each cell shows saturation at $100~cm^2$. Further widening of the cell does not affect the increase in the specific energy of the cell. With respect to the thickness of cell, depending on the thickness of cathode, each cell shows different critical number of bipolar units which show saturation. The specific energy values show limitations at 100, 40, 10 of bipolar units for 1,10, 100 and $100~\mu m$ -thick cathodes.

In Fig.13, specific energy of the same cells are plotted against cathode thickness which ranges from 1 μ m to 100 mm. The number of bipolar unit(X)=0 curve represents the results for a unit cell, and the other curves ($X\geq 1$) for bipolar configurations with the number of bipolars up to 100. However as the bipolar units becomes larger, the cell shows high specific energy even for decreased thickness. The value for bare cell elements (anode, cathode, and electrolyte) without any hardware is also shown in this figure.

Specific Power

In Fig.14, specific power of the same bipolar-configuration Li/LiClO4(PC)/PAn cell is shown as a function of number of bipolar unit. Like specific energy variation, the values show saturation at the same numbers of bipolar cells. Also, with respect to surface area, the values do not change very much over 100 cm². However, the specific power value changes dramatically with varying cathode thickness, and the range of values is determined by the range of cathode thickness.

CONCLUSIONS

Specific energy and power show reverse trends with respect to the thickness of cathode. It is suggested that we can not maximize high values for both specific energy and power for the same cell thickness. So, we have to sacrifice either energy or power depending on the thickness of the cell. As this type of polymer cathode system yields extremely high power compared to relatively high energy, the cell may be better designed to have a thinconfiguration of about 100 µm for optimized performance. Finally, the best cell design suggested by Fig.15 has 62 MW/kg for a 1mm-thick cathode with 100-bipolar cell. A maximum of 100 Wh/kg can be attained for 10-bipolar unit 100 µm-thick cathode cells.

ACKNOWLEDGEMENT

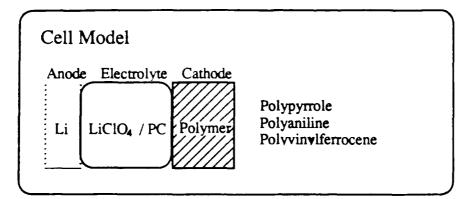
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List of Symbols

Symbol	Unit	Notation
В	mol dm ⁻³	Initial, concentration of electrolyte at fully discharged state
d _a	g cm ⁻³	Density of anode
dc	g cm ⁻³	Density of cathode
dcase	g cm ⁻³	Density of synthetic. resin case
d _{oc}	g cm ⁻³	Density of current collector(Al) in a bipolar unit
doct	g cm ⁻³	Density of current collector(Ni) at terminals
d _e	g cm ⁻³	Density of electrolyte(3M LiClO ₄ /PC)
d _{solv}	g cm ⁻³	Density of solvent (PC)
E _{ave}	V	Average discharge voltage
E _{OC}	v	Open circuit voltage of 1 bipolar unit
ED ED	Wh kg ⁻¹	Energy density per cell
f _{ex}	-	Excess factor of anode to cathode
La	cm	Thickness of anode
L_c	cm	Thickness of cathode
L_{cc}	cm	Thickness of current collector in a bipolar unit
L _{cell}	cm	Thickness of active cell
L_{cct}	cm	Thickness of current collector at terminal
Le	cm	Thickness of electrolyte
L*	cm	Thickness of total cell
Ma	g mol ⁻¹	Molecular weight of anode (Li)
M_c	g mol ⁻¹	Molecular weight of cathode
Msalt	g mol ⁻¹	Molecular weight of salt (LiClO ₄)
Pmax	W unit $^{-1}$	Max. power of 1 bipolar unit
PD _{rnax}	$W g^{-1}$	Power density per cell
S	cm ²	Area of active cell
S_{cc}	cm ²	Area of current collector in a bipolar unit
Scct	cm ²	Area of current collector, terminal (=S _{cc})
V_a	cm ³	Volume of anode in a bipolar cell
v _c	cm ³	Volume of cathode in a bipolar cell
V _{cell}	cm ³	Volume of active cell unit
V _e	cm ³	Volume of electrolyte in a bipolar cell
W _a	g	Weight of anode in a bipolar unit
W _c	8	Weight of cathode in a bipolar unit
Wcase	g	Weight of case
W _{cc} *	g	Weight of current collector in a whole cell
Wcell	g	Weight of active cell in 1 bipolar unit
Wcell*	g	Weight of total cell
We	g	Weight of electrolyte in a bipolar unit
X	-	Number of bipolar unit
Уmax	%	Max. doping level of polymer cathode
ρ	Ω cm	Resistivity of LiClO ₄ /PC



Cell Reaction for Li/LiX/PPy cell

Cathode
$$x^- + e^- = n$$
 $+ x^-$

Anode $x^- + e^- = n$

$$x^- + e^- = n$$

$$x$$

Fig. 1 Cathode and anode reactions of Li/LiClO₄/Polypyrrole cell

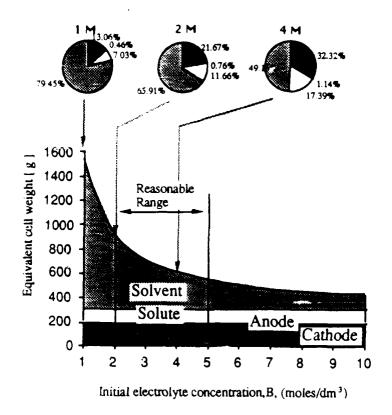


Fig. 2 Total equivalent cell weight(1 Faraday) of Li/B mol dm⁻³ LiClO₄(PC)/PPy as a function of initial concentration, B of electrolyte

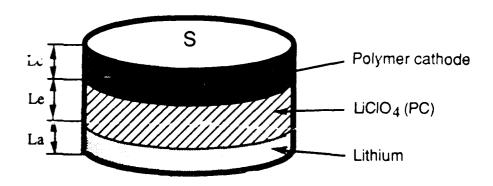
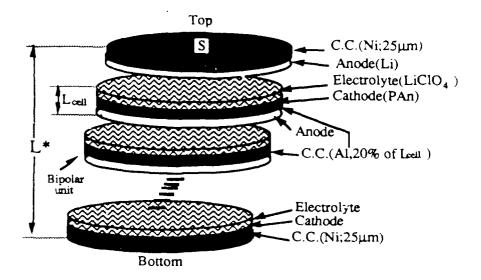


Fig. 3 Cell Construction for unit cell without hardware



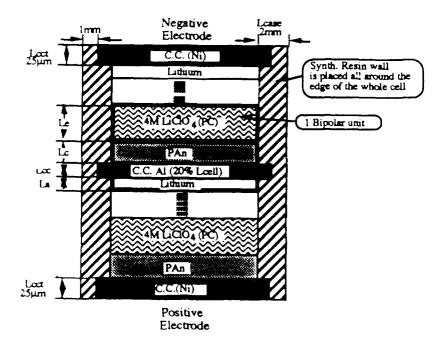


Fig. 4 Bipolar cell construction(top) for Li/4 M LiClO₄(PC)/PAn cell, and the cross-sectional view(bottom) of the bipolar unit.

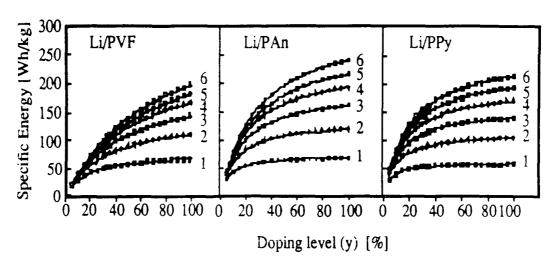


Fig. 5 The effect of doping level and salt concentration(1-6 M) on specific energy of lithium/polymer cathode cells, number in the figure indicates the molarity of electrolyte solutions.

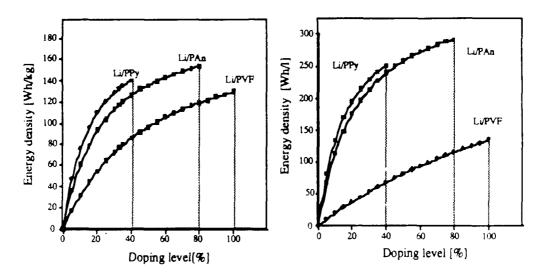


Fig.6 Gravimetric(left) and volumetric(right) energy densities for three types of Li/LiClO₄(PC)/Polymer cells.

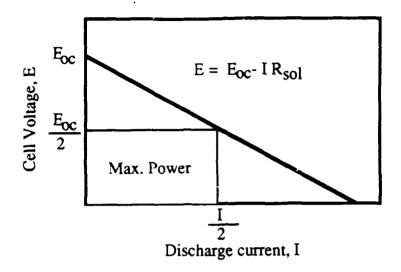


Fig.7 Cell voltage vs. Discharge current relationship(load curve)

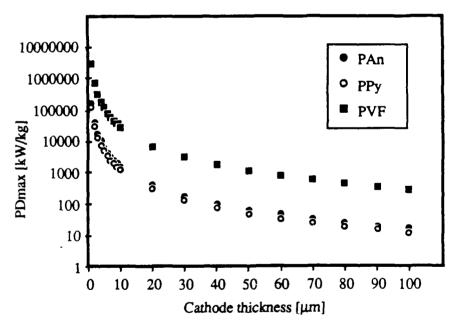


Fig.8 PD_{max} vs. cathode thickness for Li/4M LiClO₄(PC)/Polymer cell

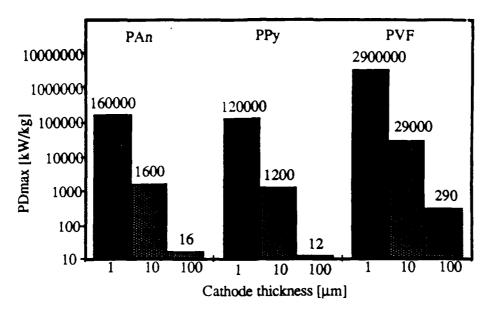
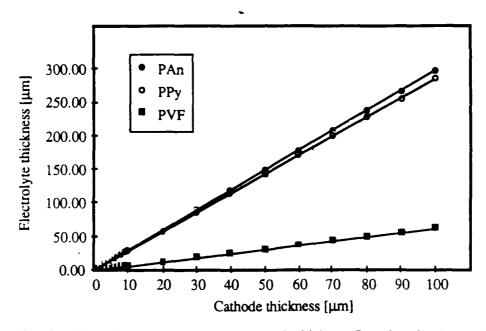


Fig.9 Comparison of PD_{max} values for Li/4M LiClO₄(PC)/Polymer cells



 $\label{eq:Fig.10} Fig.10 \quad Electrolyte \ thickness(L_e) \ vs. \ cathode \ thickness(L_c) \ plots \ for \ three \ polymer \\ cathode \ systems$

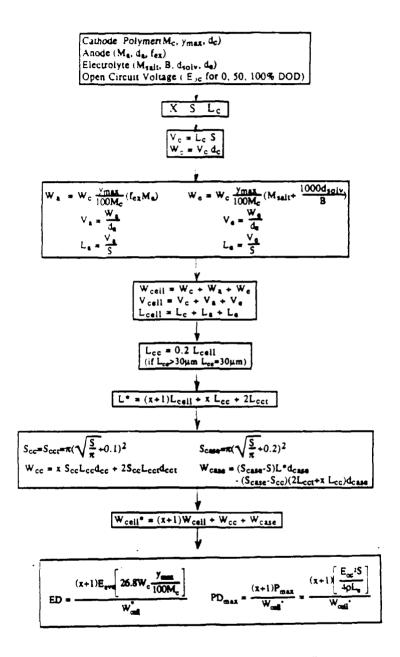


Fig.11 Calculation procedure of specific energy, specific power and cell weight for bipolar-design Li/4M LiClO₄(PC)/PAn cell.

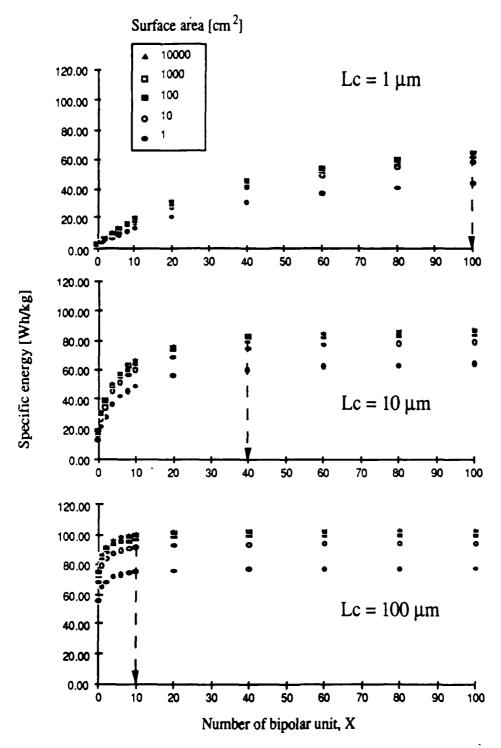


Fig.12 Specific energy vs. number of bipolar unit for bipolar-design Li/LiClO₄(PC)/PAn cells, where the cathode thickness is varied from 1 to 100 μ m.

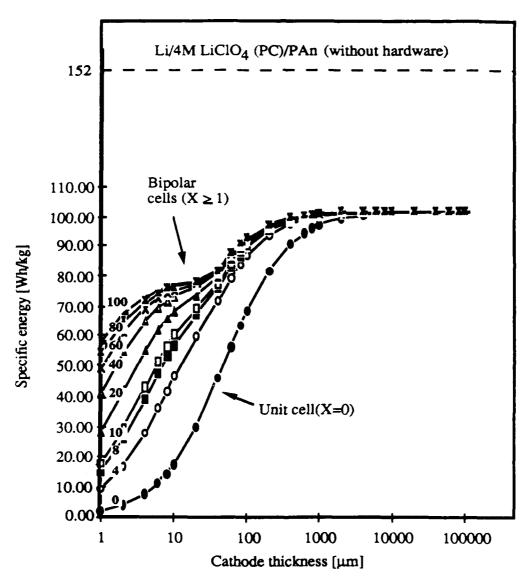


Fig.13 Specific energy vs. cathode thickness plots for bipolar-design Li/PAn cells.

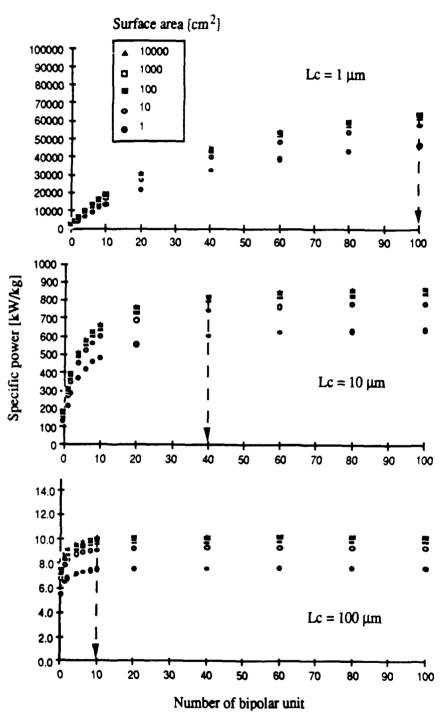


Fig.14 Specific power vs. cathode thickness for bipolar Li/PAn cells

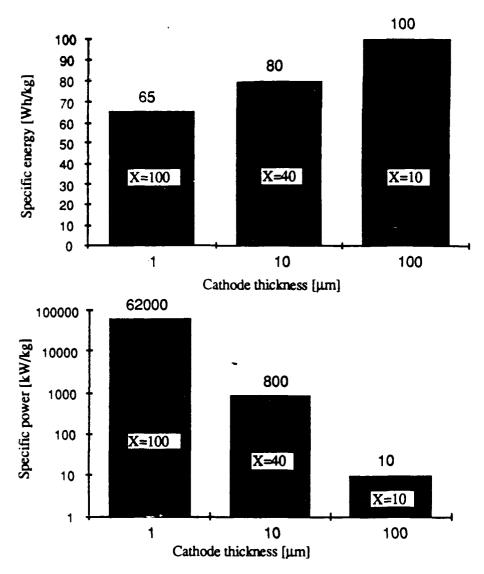


Fig.15 Optimal values for specific energy and power for bipolar-design Li/4M LiClO4(PC)/Polyaniline cells with various cathode thicknesses, viz., 1, 10, 100 μm ; S=100 cm²

Key Words

Page 1	Energy density, power density, lithium battery, conductive polymer
Page 2	Cell model, equivalent weight
Page 3	polypyrrole, polyvinylferrocene, polyaniline, pulse power
Page 4	Bipolar battery, hardware
Page 5	Polymer cathode system, optimization, cell performance
Page 6	List of symbols
Pages 7-17	Figures